

Resonant and nonresonant x-ray emission spectroscopy of poly(pyridine-2,5-diyl)

M. Magnuson, J.- H. Guo, C. S  the, A. Agui and J. Nordgren

Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden

Introduction

Conjugated polymers have been the subject of much interest owing to their unique electronic properties which can be technically exploited e.g., as doping induced electrical conductors and light emitting diodes [1]. Detailed experimental studies of the uppermost π -orbital levels at the valence band edges of these polymers are important to gain an understanding of their properties. Such studies have been carried out by many techniques including photoelectron spectroscopy using photon excitation in both the x-ray and ultraviolet wavelength regimes.

X-ray emission spectroscopy (XES) provides a useful technique for studying conjugated polymers but has yet not been exploited much. XES provides a means of extracting electronic structure information in terms of local contributions to the Bloch or molecular orbitals (MO's), since the x-ray processes can be described by local dipole selection rules. The method is atomic element specific and also angular momentum and symmetry selective at high resolution. However, the relatively low fluorescence yield and instrument efficiencies associated with x-ray emission in the sub keV region places considerable demands. An intense synchrotron radiation (SR) excitation source is therefore required which has earlier limited the experimental activity of studying the behavior for radiative emission spectroscopy of oligomers and polymers.

The nonresonant x-ray emission spectra are obtained when the energy of the incident photons exceed far above the core ionization threshold. In this case the x-ray emission spectral profile is practically independent (besides x-ray satellites) of the excitation energy and has been often described using a two-step model with the emission step decoupled from the excitation step. On the other hand, when the excitation energy is tuned at resonances below or close to the core ionization threshold, the spectral distribution is strongly dependent on the excitation energy. The description in the resonant case must therefore switch from a two-step to a one-step model with the excitation and emission transitions treated as a single scattering event in resonant inelastic x-ray scattering (RIXS).

In a recent work we used a set of poly(*p*-phenylenevinylene)s; PPV, PMPV and PDPV to demonstrate the feasibility of studying the electronic structure of conjugated polymers by means of resonant and nonresonant x-ray emission with monochromatic SR excitation [2]. It is of interest to find out how the resonant and non-resonant spectra show up in more complicated hetero-compounds, then also mapping the energy bands by transitions from more than one atomic element. In this present work we present, and analyze for this purpose, the x-ray emission spectra of poly(pyridine-2,5-diyl) (PPy) which is an aza-substituted poly(*p*-phenylene). The analysis based on *ab initio* canonical Hartree-Fock theory indicate isomeric dependence of the carbon x-ray absorption spectra and the resonant x-ray emission spectra [3]. The resonant emission spectra also show that the π electron bands disappear in the spectra due to symmetry selection and momentum conservation rules.

Experiment

The experiments were carried out at beamline 7.0 at ALS. This undulator beamline includes a spherical-grating monochromator and provides linearly polarized SR of high resolution and high brightness. X-ray absorption (XA) spectra were recorded by measuring the total electron yield from the sample current with 0.25 eV and 0.40 eV resolution of the beamline monochromator for the carbon and nitrogen edges, respectively. The XA spectra were normalized to the incident photon current using a clean gold mesh in front of the sample.

The x-ray emission spectra were recorded using a high-resolution grazing-incidence x-ray fluorescence spectrometer [4]. During the x-ray emission measurements, the resolution of the beamline monochromator was the same as in the XA measurements. The x-ray fluorescence spectrometer had a resolution of 0.30 eV and 0.65 eV, for the carbon and nitrogen measurements, respectively. The energy scale has been calibrated using the elastic peak in the x-ray emission spectra which has the same energy as the incoming photon energy. The sample was oriented so that the incidence angle of the photons was 20 degrees with respect to the surface plane. During the data collection, the samples were scanned (moved every 30 seconds) in the photon beam to avoid the effects from photon-induced decomposition of the polymers. The base pressure in the experimental chamber was 4×10^{-9} Torr during the measurements.

Results

X-ray emission and absorption at the N $1s$ threshold

Figure 1 shows resonant (bottom) and non-resonant (top) X-ray emission spectra of PPy excited at 398.8 eV and 408.3 eV photon energy, respectively. In the XA spectrum (dashed lines) an intense peak at about 398.8 eV corresponds to absorption from the core to the π^* lowest unoccupied

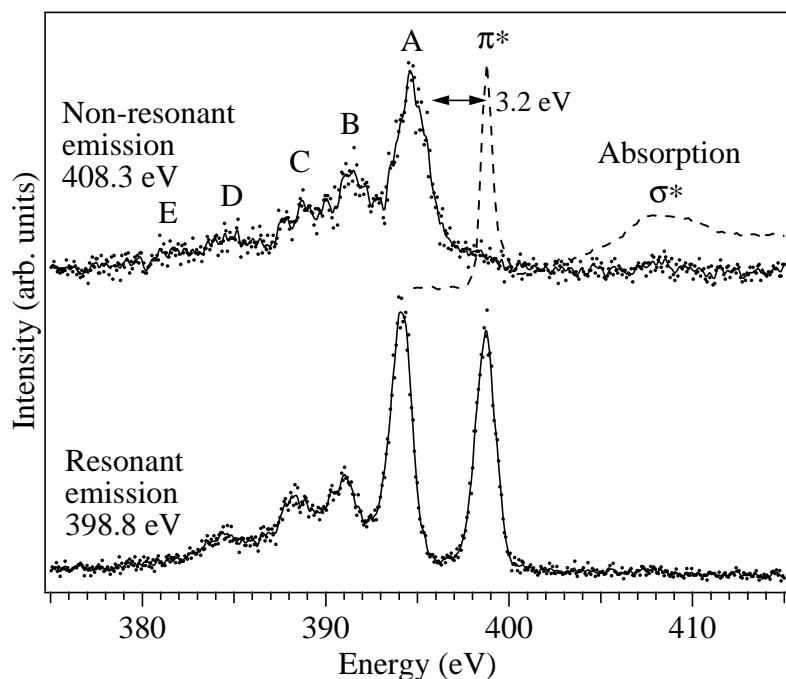


Fig. 1: X-ray emission and absorption spectra of PPy at the N $1s$ threshold.

molecular orbital (LUMO). At higher photon energies, broad shape resonances are observed mainly due to absorption from core to the unoccupied σ^* MO's and multielectron processes. The shape and position of the absorption features are connected to the final core excited state.

In the resonant emission spectrum a strong elastic (recombination) peak is observed at 398.8 eV. In both the emission spectra, five features (labeled A-E) can be observed. Peak A corresponds to π -electron states at the valence band edge and peak C corresponds to σ electronic states. In the resonant case the band structure is similar to the non-resonant case.

X-ray emission and absorption at the $C1s$ threshold

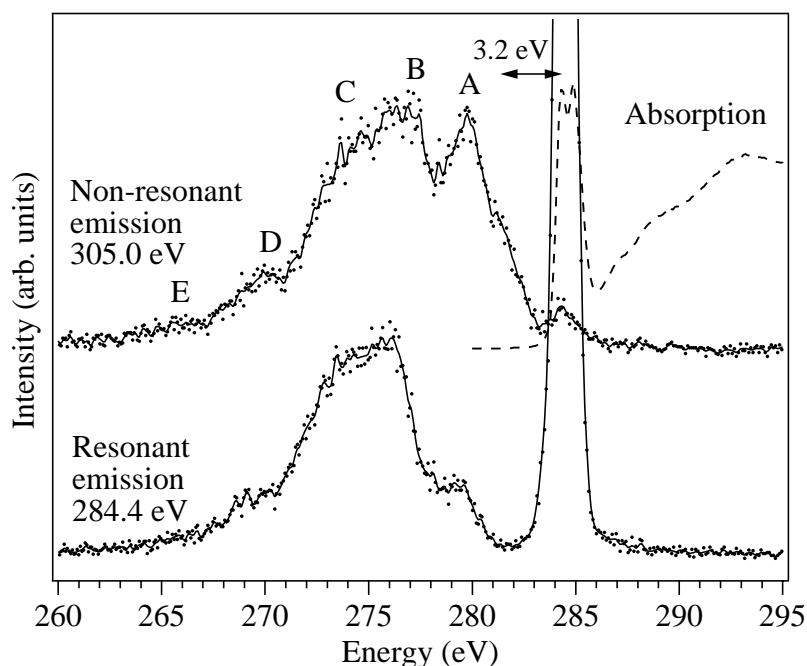


Fig. 2: X-ray emission and absorption spectra of PPy at the $C1s$ threshold.

Figure 2 shows resonant (bottom) and non-resonant (top) x-ray emission spectra of PPy excited at 284.4 eV and 305.0 eV, respectively, and an x-ray absorption spectrum (dotted lines) measured at the carbon $1s$ threshold of PPy. A double peak structure in the absorption spectrum with peaks at 284.4 eV and 285.0 eV, corresponds to the lowest unoccupied molecular $C1s$ (LUMO) orbitals which are chemically shifted. At higher energies, similar broad shape resonances as in the nitrogen case are observed in the carbon absorption spectrum.

The x-ray emission spectra of carbon obviously map the same final levels as the nitrogen spectra but with a different energy scale and transition moments owing to

the different intermediate states. The non-resonant x-ray emission spectrum is dominated by the $2p \rightarrow 1s$ diagram transitions between the valence and core vacancy states in normal emission. A peak with lower intensity is clearly visible at 284.5 eV due to multielectron satellite transitions.

Discussion

In the C K spectra the MO's of band B have more intensity than in the nitrogen spectra due to a stronger contribution from the carbon atoms as these MO's have a larger dipole overlap with the $C1s$ core orbitals than with the $N1s$ core orbitals. For the inner MO's, such as band E, the intensities are weaker in both the C and N K spectra due to the larger $2s$ character of the MO's. Thus, while the carbon spectra show a similar peak structure of the bands, the intensity distribution is different. In both cases the resonant spectra show strong elastic (recombination) peaks. Comparing the resonant and non-resonant C K spectra, the largest difference occurs at about 280 eV photon energy, where band A appears only as a weak feature in the resonant spectrum. The vanishing of the A-band has previously been observed for resonant x-ray emission spectra of benzene [5] and is the result of the parity selection rule. In previous studies of aniline [6] and poly(*p*-phenylenevinylene) polymers [2], it was argued that the *multi-channel interference* effects make transitions from π MO's of the A-band to the $C1s$ core orbitals effectively forbidden. Thus the interference effect, and so the symmetry selectivity, grows progressively stronger as the chemical disturbance of the benzene rings becomes weaker. Hence, the A-band emerges only as a weak feature the spectra. Just as the symmetry selection in the resonant aniline spectrum the momentum conservation for resonant emission in the polymers is an effect of channel interference. For π conjugated polymers this momentum conservation leads to depletion of emission from π -levels, as nicely confirmed in the present work

[3] and in ref. [2] for the PPV compounds. One finds the depletion to be about as strong for PPy as for PPV compounds although one would expect a smaller effect for PPy due to the stronger chemical shifts of the core-excited states. However, we do not observe a corresponding depletion going from the non-resonant to the resonant condition in the nitrogen spectra. This is explained by the fact that the strong high-energy band in these spectra are due to the lone-pair n orbitals, localized on the nitrogen sites, which have σ symmetry. The different localization character of the emitting levels are clearly revealed from the analysis of the resonant spectra. By subtracting the energy of this edge structure in the non-resonant spectrum from that of the elastic peak of the resonant spectrum provides an alternative way of experimentally obtaining the optical band gap as demonstrated in the PPV paper [2]. The band gap obtained for PPy in this way is 3.2 eV which agrees fairly well with the value of 3.05 eV obtained from ultraviolet photoelectron spectroscopy [7] and optical absorption measurements.

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Principal investigator: E. Joseph Nordgren, Physics Department of Uppsala University, Sweden.
E-mail: joseph@fysik.uu.se, Phone +46 18 471 3554.